Aging and memory effects in β-hydrochinone-clathrate

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The out-of-equilibrium low-frequency complex susceptibility of the orientational glass methanol(73%)-β-hydrochinone-clathrate is studied using temperature-stop protocols in aging experiments . Although the material does not have a sharp glass transition aging effects including rejuvenation and memory are found at low temperatures. However, they turn out to be much weaker, however, than in conventional magnetic spin glasses.

75.50.Lk,77.22.Gm,75.40.Gb,64.70.Pf

I. INTRODUCTION

Disordered and frustrated systems have attracted considerable attention during the past decade. Much effort in the recent years has been devoted to investigations of slow dynamics in these systems. Structural glasses, magnetic spin glasses and their electrical pendant, orientational glasses are the typical examples of out-of-equilibrium systems. The most remarkable and common peculiarity of these materials is physical aging as has been extensively studied in spin glasses[1] and also observed in orientational glasses (for instance $K_{0.989}Li_{0.011}TaO_3$[2,3]) and disordered ferroelectrics (for instance $KTa_{0.973}Nb_{0.027}O_3$[4]).

Recent experiments on the insulating (Heisenberg-like) spin glass $CdCr_{1.7}In_{0.3}S_4$, showed that spin glasses can even memorize some of the features of the way in which the system has been prepared[5]: Prolonged aging at a constant temperature T_1 during slow cooling, a so-called temperature-stop, causes a dip around this temperature in the temperature dependence of the imaginary part of the magnetic susceptibility upon reheating. Even multiple aging temperatures T_i can be memorized in a corresponding multi-temperature-stop experiment[6]. Other materials, like an Ising spin glass $Fe_{0.5}Mn_{0.5}TiO_3$[7], an interacting Fe-C nanoparticle system[8] and the disordered ferroelectrics $Pb(Mg_{1/3}Nb_{2/3})O_3$[9] and $KTa_{0.973}Nb_{0.027}O_3$[4] displayed similar but less pronounced memory features in these temperature stop experiments.

Whereas many aging features of disordered materials in general and of spin glasses in particular are theoretically quite well understood on a phenomenological and on the mean-field level[10], the theoretical status for these memory experiments is less clear. Two ingredients appear to be important: 1) A pronounced sensibility of the spin glass state with respect to temperature changes to explain so-called rejunvenation effects when the temperature is changed during aging (sometimes also called *chaos* in spin glasses[11]), and 2) strongly coupled regions in equilibrated domains whose once developped correlations are hard to destroy when the temperature is changed and which can serve as a nucleation centers when the temperature is raised again to explain the memory effect. Obviously such features are absent in for instance pure ferromagnets, which neither show rejuvenation effects when the temperature is changed during domain growth nor memory effects. However, strongly disordered ferromagnets display a very weak form of memory which is commonly attributed to the reconformation of domain walls upon temperature changes[12]. Loosely speaking one might summarize the current status of the theoretical picture as: The walls are the glassy objects in random ferromagnets, whereas spin glass domains behave glassy as a whole, in particular because they are most probably fractal objects[13] and surface (wall) as well as bulk contributions to aging effects are comparable. Thus is varying strength in which the materials mentioned above display the chaos and memory effect in aging experiments can be interpreted as an indication for the degree in which aging can actually be described by a simple domain growth like in random ferromagnets or random field systems, see for instance the discussion in 2.

From this viewpoint we discuss in this paper the electric dipole "pseudospin" glass system methanol(x = 73%)-β-hydrochinone-clathrate. It does not have a sharp transition temperature, glassy features become simply more and more pronounced as the temperature is decreased, similar to two-dimensional magnetic spin glasses[14], which shows strong aging effects at low temperature but do not have a spin glass transition. We demonstrate that the clathrate we study even displays at low temperatures a rejuvenation and memory effect in one-temperature-stop experiments and also a weaker effect in two-temperature-stop experiment. The paper is organized as follows: In section II we discuss some of the physical properties of the methanol-clathrate that we studied, section III deals with a number of experimental details. In section IV we present our results on temperature-stop aging experiments and in section C we discuss our findings on the background of the current theoretical understanding of aging in disordered and glassy systems.

II. THE MATERIAL

In this paper we present results on the aging and memory phenomena observed in the low frequency ac-permittivity of dipolar glass system methanol($x = 73\%$)-β-hydrochinone-clathrate. In the β-modification the quinol (HO-C_6H_4-OH) molecules form a H-bonded rhombohedral $R\overline{3}$ lattice with nearly spherical cavities, one per unit cell[15]. The methanol guest molecules residing in these cavities are bound to the quinol host lattice by weak dispersion forces, only. Therefore, they can reorient relatively freely. At 65 K the methanol(97%)-clathrate shows an antiferroelectric transition[16]. The structure consists basically of ferroelectric chains running along the hexagonal axis which are arranged in sheets of alternating sign. Similar phase transitions have been observed also for other polar guest molecules. Matsuo and Suga[17] have found the transition temperature T_s to scale with square of the dipole moment μ of the free molecules. It thus suggests that the dominant coupling between the guest molecules is the electrostatic dipole-dipole interaction. Higher concentrated samples ($x > x_c \approx 0.76$) of methanol(x)-β-hydrochinone-clathrate show conventional ordering via a first-order phase transition, whereas the others ($x < x_c$) freeze into dipole glasses.

Woll *et al*[16] have studied the dielectric relaxation as a function of temperature, frequency and methanol concentration. The static dielectric constant along hexagonal c-axis ε_{cs} shows strong deviation from the Curie-Weiss behavior already at 250 K. The temperature dependence of ε_{cs} at higher temperatures is well described within mean-field approximation by the one-dimensional (1D) Ising model with a coupling J_c to nearest neighbors within the chain and an inter-chain interaction with coupling constant $J_\perp$. The coupling constants are consistent with the electrostatic dipole-dipole interaction, the elementary dipole moments being practically identical with that of the free methanol molecule. At lower T, $\varepsilon_{cs}(T)$ deviates from the Ising-behavior and finally decreases with decreasing T, indicating the onset of 3D antiferroelectric inter-chain correlations. Such a behavior persists also for samples with lower concentrations of methanol: the static dielectric constant possesses a broad maximum in the region of about 55 K. For samples with a higher concentration, 3D-correlations eventually lead to the antiferroelectric phase transition. For samples with lower concentration the antiferroelectric fluctuations presumably prevent total ferroelectric ordering. Accordingly, in the low-temperature region one can expect the coexistence of different types of locally ordered regions, i.e. clusters of polar and antipolar types. The dielectric relaxation therefore depends strongly on the dynamics of polarization clusters in an ac-field.

As it was shown before[16], the relaxation processes are characterized by rather broad distribution of relaxation times τ, which is typical for disordered systems. In Fig. 1 the inverse average relaxation time is plotted against the inverse temperature in a log-linear plot. The data lay on a straight line which implies an Arrhenius law

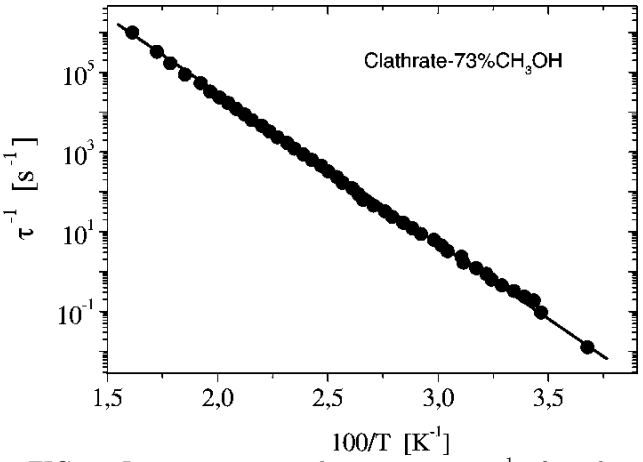

FIG. 1. Inverse average relaxation time τ^{-1} of methanol (73%)-clathrate as a function of $1/T$.

$$\tau^{-1} \sim f_0 \exp(-E_A/T) \tag{1}$$

rather than a Vogel-Fulcher behavior $\tau^{-1} \sim f_0 \exp(-E_A/(T - T_{vf}))$ as in structural glasses[20] or critical slowing down $\tau^{-1} \sim (T - T_c)^{z\nu}$ in spin glasses[21]. In spin glasses the critical temperature T_c at which the relaxation time diverges is identical to the spin glass transition temperature at which the non-linear susceptibility and hence the spin glass correlation length diverges. In structural glasses the Vogel-Fulcher temperature T_{vf} can serve as a lower bound for the strongly cooling rate dependent concept of a glass transition temperature. Fig. 1 tells us that our methanol (73%)-clathrate does *not* show a well defined glass transition in the temperature range 25-100K, the dynamics simply gets slower with decreasing temperature according to (1). It therefore differs strongly from other popular examples of dipolar glasses, e.g. $Rb_{1-x}(NH_4)_xH_2PO_4$[18] (member of KDP family) or cubic perovskites, such as $K_{1-x}Li_xTaO_3$[19]. Nevertheless the freezing of the dipole moments of the 73% clathrate is to some part a collective process. Not only the crystal field of the cavity, but also the interaction between the dipoles contribute to the Arrhenius barrier E_A in (1). As we will demonstrate in this paper, aging, rejuvenation and memory phenomena are observable in the aformentioned temperature range.

III. EXPERIMENTAL DETAILS

The single crystal of methanol(73%)-clathrate has been grown from a saturated solution of quinol, methanol and n-propanol at 313 K. The sample was prepared in the form of a thin parallel plate ($d \approx 0.5$ mm). The faces were oriented perpendicular to the hexagonal c-axis. Gold films deposited on these faces serve as electrodes. The real and imaginary part of the dielectric constant

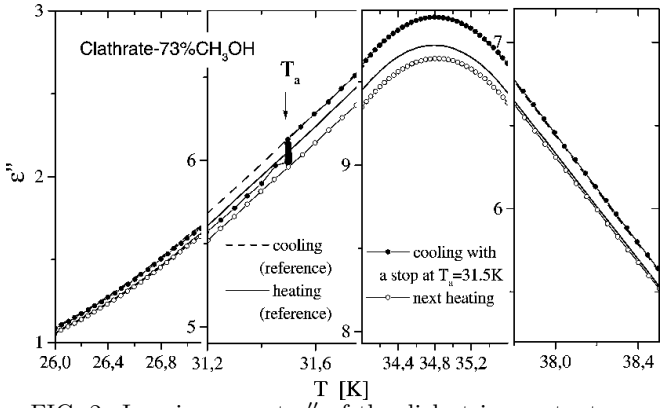

FIG. 2. Imaginary part ε'' of the dielectric constant measured at 2 Hz in methanol(73%)-clathrate. Shown are the reference curves $\varepsilon''_{ref}(T)$ for continuous cooling and heating with $|dT/dt|$ of about 0.1 K/min and the data for the single temperature-stop (at $T_a = 31.5K$ for about 14h) aging experiment.

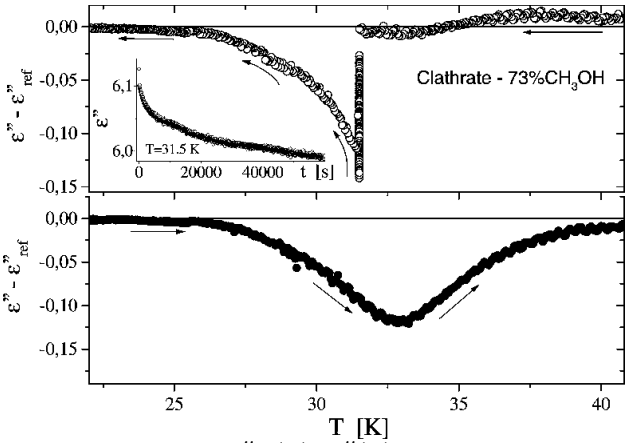

FIG. 3. Difference $\varepsilon''_{ref}(T) - \varepsilon''(T)$ calculated from the data presented in Fig.2. Insert shows the long-time relaxation of ε'' recorded at $T = T_a = 31.5$K

$\varepsilon^*(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$ are directly related to the capacitance and loss. The geometrical capacitance as calculated from the thickness and electrode area was 0.3pF

The complex dielectric constant was measured with a frequency response analyzer "Solatron" SI-1255 covering a frequency band from 0.1 mHz to 10 MHz. The amplitude of ac-field was about 50 V/cm. Measurements of the electric polarization P as function of the electric field E along the hexagonal axis show perfect linear behavior up to the maximum field of about 40 kV/cm. It assures that the measured susceptibility clearly appears in the frame of the linear response. The samples were placed into a He-flow cryostat with a stability of the temperature control of about 0.002 K.

IV. TEMPERATURE STEP EXPERIMENTS

Motivated by recent aging and memory experiments on spin glasses[5] we performed aging and memory experiments on methanol(73%)-clathrate using the following temperature protocol. First reference curves are recorded as a function of temperature at rather slow cooling and heating ($|dT/dt|$=0.1-0.3 K/min). In the aging experiment the sample is then continuously cooled with the same speed, but is additionally kept at a certain constant temperature T_a for a waiting time of several hours. The ac-susceptibility χ relaxes downwards (aging effect) but upon a subsequent cooling it approaches its reference value at somewhat lower temperature $T = T_a - \Delta T$ (rejuvenation). During the next re-heating the temperature dependence $\chi(T)$ shows a broad dip in the vicinity of T_a, which, of course, does not exist in the reference curve. Accordingly, the system "remembers" its aging temperature T_a (memory effect). This anomaly completely disappear after overheating for a few degrees above T_a, so subsequent temperature cycling around T_a shows again the reference behavior.

Fig. 2 shows such a sequence of several cycling experiments. The results are presented only for a few temperature intervals, which have different vertical scales. This unusual presentation is necessary in order to make the smlaa differences at the various traces visible. The reference behavior of $\varepsilon''(T)$ are first recorded as a function of temperature at cooling/heating rate $|dT/dt|$ of about 0.1 K/min. One can see that the reference curve $\varepsilon''_{ref}(T)$ at heating is always somewhat lower than at cooling thus clearly indicating on an out-of-equilibrium behavior. However, if cooling is interrupted for a time t_a (in our experiment $t_a \approx 50$ ks) at constant temperature (e.g. $T_a = 31.5$ K) the imaginary part ε'' decreases by the effect of aging. Upon a subsequent cooling $\varepsilon''(T)$ approaches its reference value ε''_{ref} at somewhat lower temperature of about $T \approx 25K$. During the next reheating the temperature dependence $\varepsilon''(T)$ shows a little bit lower value than reference. This difference again disappears at subsequent cooling-heating cycles.

In order to highlight the consequences of isothermal aging (Fig. 2) it is quite convenient to present the data as difference between the curves recorded during the second and the first (reference) cooling-heating circles (see Fig. 3). One can clearly see the sequence of the several effects: aging at $T = T_a$ with long-time evolution (see insert in Fig. 3), the rejuvenation upon the subsequent cooling and the memory effect at further re-heating leading to the broad dip centered close to the aging temperature T_a. Quite similar behavior has been recently reported in disordered ferroelectric $KTa_{0.973}Nb_{0.027}O_3$[4]; the authors have presented their results in the same manner as in the Fig. 3. In fact, the data presented in differential form are not able to give true impression about the aging behavior. For example, the rejuvenation observed at the low temperatures in methanol-clathrate could be simply due to the almost complete dynamical freezing. The reference curve $\varepsilon''_{ref}(T)$ approaches in this temperature range its zero level and since

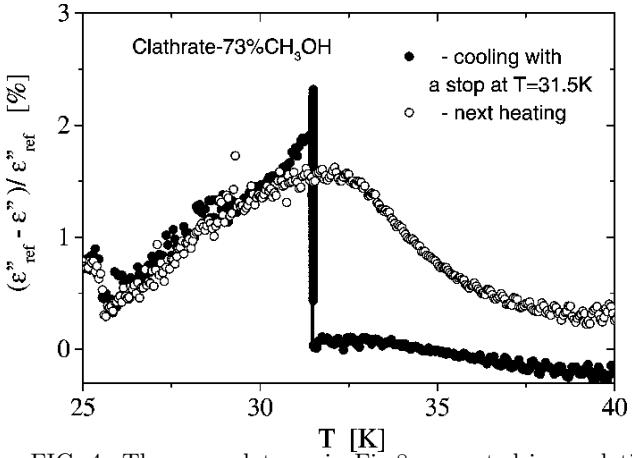

FIG. 4. The same data as in Fig.8 presented in a relative form (i.e. $e = (\varepsilon''_{ref}(T) - \varepsilon''(T))/\varepsilon''_{ref}(T)$ vs the temperature).

$\varepsilon''_{ref}(T) > \varepsilon''(T)$ the difference $\varepsilon''_{ref}(T) - \varepsilon''(T)$ will always have the same tendency. In order to avoid this problem one must present the data in a relative form, i.e. as $e(T) = (\varepsilon''_{ref}(T) - \varepsilon''(T))/\varepsilon''_{ref}(T)$ vs. the temperature. The corresponding dependence is shown in Fig. 4.

Fig. 5 and Fig. 6 present so-called double- aging/memory experiment: the cooling process was interrupted twice at the temperatures $T_{a1} = 31.5$ K and $T_{a2} = 29$ K for a time $t_{a1} = t_{a2} = 50$ ks. For both temperatures the imaginary part ε'' decreases by the effect of aging. Upon a subsequent cooling one can see rejuvenation, whereas during the re-heating the temperature dependence $\varepsilon''_{ref}(T) - \varepsilon''(T)$ shows again a broad maximum. Two anomalies which are expected to occur due to the memory effect are not well separated in our case. The temperature interval ($\Delta T = T_{a1} - T_{a2} = 2.5$ K) is too small for that, and additionally, the aging and memory at the lower temperature T_{a2} are characterized by much weaker anomalies. Nevertheless, one can see some difference in the temperature dependence $\varepsilon''_{ref}(T) - \varepsilon''(T)$ obtained during the heating in the single-aging(see Fig. 5, line) and double-aging (points) experiments. Both these effects are much more pronounced when presented as relative changes in Fig. 6. We note that similar observation of the double-aging/memory effects was recently reported in[4] for $KTa_{0.973}Nb_{0.027}O_3$ crystals. By choosing of a larger temperature interval between the aging temperatures (of about 5 K), authors obtained here two well separated dips corresponding to the memory effect.

V. DISCUSSION

Since spin glasses, in contrast to structural glasses, have an order parameter, the EA-order parameter, it appears natural to interpret aging phenomena at low temperatures in terms of a slowly increasing domain length — indications for this have been found numerically in microscopic SG models[22] as well in recent

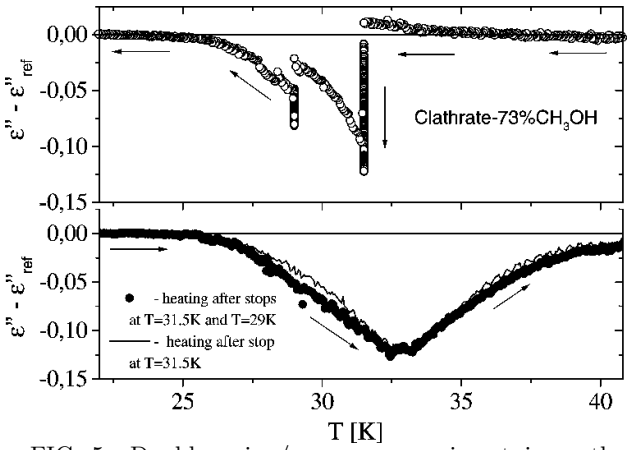

FIG. 5. Double aging/memory experiment in methanol (73%)-clathrate. The dependence $\varepsilon''_{ref}(T) - \varepsilon''(T)$ vs. the temperature is shown for cooling and heating runs. The experimental procedure is similar to this, which is described in Fig.7 with the difference only that the second cooling run was twice interrupted at the temperatures $T_{a1} = 31.5$ K and $T_{a2} = 29$ K for the time of about 50 ks in each case.

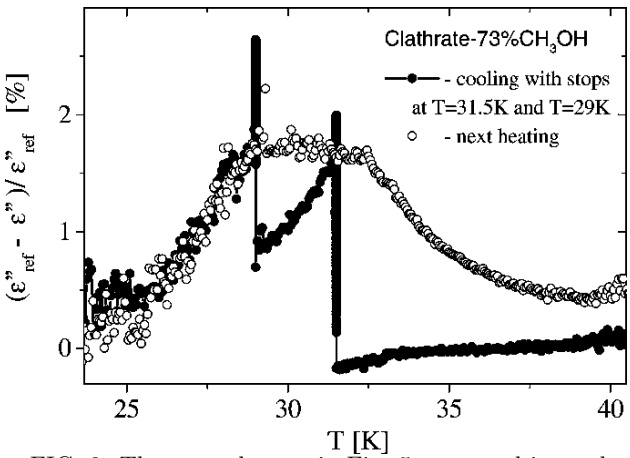

FIG. 6. The same data as in Fig. 5 presented in a relative form (i.e. $e = (\varepsilon''_{ref}(T) - \varepsilon''(T))/\varepsilon''_{ref}(T)$ vs. the temperature).

experiments[23]. A simple domain growth, however, cannot explain the memory effect as evidenced in these multiple-temperature-stop experiments: in spin glasses domains at different temperatures have to be uncorrelated to some extent, in contrast to domains in a ferromagnet for instance. This feature is often called *chaos* in reminiscence of the notion of a finite overlap length of *equilibrium* states in finite-dimensional spin glasses[11]. In addition to this temperature-chaos in spin glasses to explain the memory effect the once grown domains should also not be completely destroyed when the temperature is lowered but should retain one or several nuclei at least for times comparable to the aging time at lower temperatures — such an idea was put forward recently in[6].

Comparing the outcome of our experiments, in particular the two-temperature-stop experiments depicted in Fig. 5 and 6 with the corresponding experiments on the insulating spin glass $CdCr_{1.7}In_{0.3}S_4$[5], shows that the aforementioned spin glass features, including rejuvenation and memory, are much less pronounced. An obvious difference is of course that $CdCr_{1.7}In_{0.3}S_4$ has a clear phase transition at a temperature $T_g = 16.7K$ to a spin glass phase at (and below) which any relaxation time of the system diverges and below which the multiple-temperature-stop experiments have been performed. On the other hand, no indication of a sharp transition can be found in our clathrate although the relaxation time below 20K already exceeds the experimental time-scales accessible to us. Quite frequently aging properties of spin glasses at very low temperatures that do *not* have a phase transition at finite temperatures — like pseudo-2d materials or thin films[14] — resemble those of real spin glasses (i.e. those with a clear phase transition) in the frozen phase. It might well be that this is not so for chaos and memory, for which one actually needs to have in a spin glass phase. Another explanation of the difference could be that our orientation glass, the methanol clathrate we studied here, is less glassy than expected from other experiments[16] and resembles more the disordered dielectric $K_{1-x}Li_xTaO_3$: Here aging effects can be interpreted as a simple domain growth of varying speed and the system appears to be more closely related to a random field system rather than a spin glass. Certainly it would be worthwhile to scrutinize the details of the microscopic mechanism underlying the aging effects we presented in a more detailed form.

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